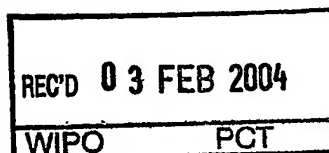


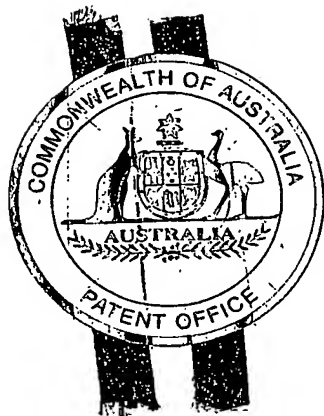
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Title: Improved Blends for Injection Moulding Flexible Thin Walled Articles

This application relates to a number of different improvements in blends suitable for the manufacture of flexible thin walled mouldings as defined in the '255 patent. All W/O and US patents cited or referred to in this document are hereby incorporated by reference.

Definitions

Blends and techniques described herein are specifically for the production of injection moulded flexible thin walled mouldings as described in the '255 patent and generally have MFIs (measured as I2) >10, preferably >20, preferably >30 and most preferably >50, but the technology and formulations described herein may also cover other applications and blends with lower MFIs.

- **'255 patent'** PCT/AU98/00255, which is hereby incorporated by reference.
- **ACA:** 'additional compatible agent' which may be either a non-polymer or polymer which is compatible with the ALOP or ALOCA. Materials capable of nucleating polymer crystallisation are typical ACAs.
- **ALOP:** 'at-least-one-polymer', which is usually the main polymer constituent(s) of a particular blend and is the polymer(s) forming the continuous phase of a blend. The ALOP has an MFI of >10, preferably >20, more preferably >30, even more preferably >50.
- **ALOCA:** 'at-least-one-compatible-agent', which may be either a non-polymer or polymer which is compatible, but not miscible, with the ALOP and usually forms or is part of the disperse phase of a blend. When the ALOCA is a polymer, it has an MFI ≤ 100 .
- **ALOHMFCA:** 'at-least-one-high-melt-flow-compatible-agent', which is an ALOCA polymer(s) having an MFI of >100 (eg. a 350 MFI PP).
- **ESCR:** The ESCR of a polymer blend when tested according to the ESCR test.
- **ESCR test:** The ESCR test as defined in the '255 patent.
- **Blend:** One or more polymers compounded together and which, in order to be suitable for tube manufacture, must pass the ESCR test as defined in the '255 patent.
- **α -olefin:** α -olefins suitable for copolymerisation with other monomers, particularly ethylene, propylene or butene, to produce ethylene, propylene or butene α -olefins suitable for the production of injection moulded flexible thin walled mouldings. These include α -olefins in the range of about 2 to about 20 carbon atoms, preferably in the range of about 3-16 carbons, most preferably in the range of about 2-8 carbon atoms. α -olefins may be saturated or unsaturated straight chained, branched chained or cyclic hydrocarbons. The '255 patent contains many examples of α -olefins suitable for use in tube polymers.
- **Polyene:** Polyene comonomers suitable for the copolymerisation with ethylene, propylene or butene to form ethylene, propylene or butene copolymers suitable for injection moulded flexible thin walled mouldings. Suitable polyenes have, in the main, about 3 to 20 carbon atoms, preferably in the range of about 4 to about 20 carbon atoms, most preferably in the range of about 4 to about 15 carbon atoms. In one embodiment the polyene is a diene that has in the range of about 3 to about 20 carbon atoms. Preferably the diene is a non-conjugated diene. Polyenes may be straight chained, branched chained or cyclic hydrocarbon polyenes. The '255 patent contains a number of examples of polyenes suitable for use in tube polymers.

- **Injection moulded flexible thin walled mouldings:** injection moulded tubes and/or other injection moulded flexible thin walled articles as described in the '255 patent.
- **Miscible polymer:** a polymer that, when compounded with an ALOP or ALOCA, does not form a separate and distinct phase within the ALOP or ALOCA, i.e. it is essentially miscible with the ALOP or ALOCA.
- **Bulk polymer:** The polymer(s) that form the continuous phase of polymer blends. Bulk polymers usually form the major percentage of a polymer blend.
- **Standardised Fill ratio:** A standardised measure of the fill rate of a tube tool, and measured in mm/sec units.

New Materials for Use in Injection moulded flexible thin walled mouldings

In addition to ALOPs and ALOCAs described in the '255 patent, a number of recent polymer developments have utility for tube manufacture. The disclosures in this document should be read with these new polymers as well as the '255 disclosures in mind.

Highly Branched Polyolefins

Recent developments in the production of highly-branched polyolefins have enabled the production of star, comb, nanogel and other similar polymers. These polymers feature a plurality of polyolefin arms linked to a polymeric backbone to provide a highly branched structure in which the properties of the highly branched structure can be conveniently tailored to the application for which the polymer is used. The choice of specific reactive polymeric backbone and/or its manner of preparation controls the branched structure as to comb, star, nanogel or structural combinations thereof. That allows for the preparation of polymers having relatively low viscosities compared to their linear counterparts at the same absolute molecular weight. These polymer types and blends made therefrom may be particularly suitable for the production of injection moulded flexible thin walled mouldings. The rheological behaviour of these polymers with controlled branching shows surprising and useful features. These polymers frequently have a zero-shear viscosity that is larger than a linear polymer of the same molecular weight. They show a rapid drop in viscosity with shear rate (large degree of shear thinning) and a plateau modulus that is at least two times lower than that of prior art linear and branched polymers. This latter characteristic is especially surprising, since ethylene polymers of various types exhibit essentially the same plateau modulus. This was thought to be intrinsic to the monomer type and not dependent on polymer architecture. The lower plateau modulus means that the comb and similar polymers are much less entangled than the linears, thus giving them such low viscosity for their molecular weight. The utility of these properties of these polymers is that they have a very low viscosity for their molecular weights under melt processing conditions and so will process much more easily than the prior art polymers. Even when added in relatively small quantities to conventional blends suitable for injection moulded flexible thin walled mouldings, they can significantly improve blend processability. US 6,355,757 and US 6,084,030 amongst other patents describe the production of polymers such as are described above.

The copolymers of the above and similar inventions have utility in blends suitable for the production of injection moulded flexible thin walled mouldings, those blends comprising the branched copolymer of the inventions at a very wide range (eg. 0.1-99.9% weight percent), but most often between 1-5%. Depending on the properties of a specific highly-branched polymer of the above inventions and the desired properties of a particular formulation, said polymer may be used as a component of the ALOP or ALOCA part of the composition of the present invention. Depending on their properties they may also be regarded as additives rather than components of the polymer portion of the present invention.

Polypropylene Developments

Developments of particular interest in this regard are the ability to make elastomeric PP homo polymers by altering the tacticity of the polymer by various means as well as the ability to produce low flex modulus PP α -olefin copolymers with relatively low percentages of α -olefin copolymers.

As examples of one of these recent developments are linear or branched isotactic polymers, particularly polypropylene and polybutene homopolymers or random copolymers which have a structure in which their tacticity varies within the range of between 25 and 60% of [mmmm] pentad concentration. This variation in tacticity is due to the statistic distribution of stereoscopic errors in the polymer chains. Such polymers are described in, amongst others, WO 01/27169 (P&G), WO 99/52955 (Rieger) and WO 99/52950 (Rieger). Similarly, propylene/ethylene copolymers of the types described in US 6525157 (ExxonMobil) are suitable for use in injection moulded flexible thin walled mouldings. It is worth noting that propylene α -olefins in which the number of Cs in the α -olefin is >4 have particular utility for packaging requiring improved cold creep resistance relative to propylene α -olefins in which the number of Cs in the α -olefin is ≤ 4 .

Also suitable for use in the manufacture of flexible thin walled mouldings are linear or branched isotactic polymers having an arbitrary or rather regular sequence of isotactic and atactic blocks within the polymer molecules, such as are described in WO/99/29749 (ExxonMobil). WO 99/2949 describes a branched polyolefin having crystalline side-chains and an amorphous backbone wherein at least 90 mole percent of the side-chains are isotactic or syndiotactic polypropylene and at least 80 mole percent of the backbone is atactic polypropylene. They may have particular utility in blends as ALOCAs or ALOHMFCAs in blends in which the ALOP is a crystalline or semi-crystalline PP. This will be particularly the case when the polymer(s) in question has a relatively low flex modulus as it acts to reduce the flex modulus of the blend with a crystalline or semi-crystalline PP ALOP, and increasing the tear resistance, flex modulus and impact resistance of the blend.

Polymers with characteristics such as are described in the abovementioned P&G, Rieger and ExxonMobil patents may be used as the ALOP or as an ALOCA or ALOHMFCA and may have either narrow or broad molecular weight distribution. Polymers such as are described above are often particularly suited to the production of flexible thin walled articles relative to the equivalent polymers of higher tacticity because their relatively reduced tacticity results in polymers with reduced rigidity and increased flexibility and elasticity. If the polymer(s) is used as an ALOCA or ALOHMFCA, it is advantageous – though not necessary – that it is used in conjunction with at ALOP that is made from the same monomer(s) as the ALOCA or ALOHMFCA because this results in greater compatibility/stability between the polymer(s) as well as allowing for easier recycling of injection moulded flexible thin walled mouldings produced from such blends. For example, if the polymer is a polypropylene homopolymer or copolymer with tacticity varying between 25 and 60% of [mmmm] pentad concentration, it can be blended with a polypropylene homopolymer or copolymer with a higher tacticity to produce a blend suitable for use in flexible thin walled articles. Alternatively, these polymers may be used in conjunction with other polymers to form blends that are suitable for use to manufacture injection moulded flexible thin walled mouldings. For example, these polymers may be blended with polyethylenes and copolymers of different types, including LDPE, MDPE and HDPE, which in turn may be manufactured using a variety of different manufacturing techniques, catalysts and copolymers such as are described in the '255 patent.

Recent developments in polypropylene polymerisation technology have application for injection moulded flexible thin walled mouldings. One such development is the ability to

produce very flexible, soft and elastic polypropylene polymers with minor percentage of ethylene copolymer and essentially no diene. These polymers have limited crystallinity due to adjacent isotactic propylene units and have a relatively low melting point. They are generally devoid of any substantial intermolecular heterogeneity in tacticity and comonomer composition, and are substantially free of diene. They are also devoid of any substantial heterogeneity in intramolecular composition distribution. The ethylene copolymer includes lower limit of 5% by weight ethylene-derived units to an upper limit of 25% by weight ethylene-derived units. Within these ranges, these copolymers are mildly crystalline as measured by differential scanning calorimetry (DSC), and are exceptionally soft, while still retaining substantial tensile strength and elasticity. Such polymers are described in US 6,525,157.

Recent developments have resulted in the synthesis of partially atactic, partially isotactic polypropylene polymers which have elastomeric properties. It is believed that in these components each molecule consists of portions which are isotactic, and therefore crystallisable, while the other portions of the same polypropylene molecule are atactic and therefore amorphous. Such polymers are suitable for injection moulded flexible thin walled mouldings, either as ALOPs, ALOCAs or ALOHMFCAs, combinations thereof or in combination with other polymers, such as polyethylenes, polypropylenes and/or α -olefin copolymers thereof. Examples of these propylene homopolymers containing different levels of isotacticity in different portions of the molecule are described by in, amongst others, U.S. Patent 5,594,080, in Journal American Chemical Society (1995), Vol. 117, page 11586, and in the Journal American Chemical Society (1997), Vol. 119, page 3635.

Additives and Blending Techniques for Blend Production

Polymer blends suitable for injection moulded flexible thin walled mouldings may incorporate a variety of additives. Examples of additional additives include further polymers, nucleating agents, pigments, dyes, fillers, antioxidants, plasticisers, oils, UV protection, viscosity modifying agents, additives capable of reacting with or absorbing deleterious chemicals such as oxygen, mould release agents and melt strength modifiers amongst others. The addition of between 0.5% and 3% of a low MW hydrogenated aliphatic resin such as poly (dicyclopentadiene) may reduce the normalised moisture vapour transmission and sometimes the O₂ transmission rate of the blend and articles made therefrom. Additives may be added to one or more components of the polymer blend or the polymer blend as a whole prior to moulding in order to modify its properties to suit specific applications or to achieve specific effects in the end product. Some or all of the components of the the polymer blend may be prepared by mixing—preferably intense mixing—so as to produce a very fine dispersion of the individual components within the matrix, followed by extrusion and chopping of the resultant polymer blend to be used in the injection moulding process of the present invention. Alternatively, the polymer blend may be provided in its component form and subjected to mixing before and during the melting of the polymer blend in the present process. It may also be prepared by a reactor process, in which the various components of the blends are polymerised sequentially or in parallel in reactor(s) – this process frequently resulting in very fine dispersions that are unable to be obtained by other means.

Because of the high injection pressures and speeds that are frequently required to produce injection moulded flexible thin walled mouldings it is advantageous—depending on the particular formulation—to add additives to the blend that improve the flow characteristics of the polymer blends under production conditions. Of particular value are additives that have the effect of reducing the resistance to flow of the polymers when they are subjected to injection moulding conditions. There are a number of suitable additives that can be added to formulations to achieve this objective. Because different polymer formulations will respond

differently to different viscosity/processing modifiers, those skilled in the art will appreciate that the determination of the most suitable additives, their level of addition and means of incorporation is best carried out by appropriate experimentation.

Advantages of metallocene-catalysed polymers

One of the advantages of ALOPs, ALOCAs and/or ALOHMFCAs that are produced by metallocene or similar catalysts is that they have significantly lower levels of low molecular weight fractions than do similar polymers produced by catalysts such as Z-N catalysts or produced by processes such as free radical polymerisation. These low molecular weight fractions may have a number of adverse effects on the properties of blends; in particular they may cause higher degrees of tackiness of the moulded products, with consequent processing and handling difficulties as well as resulting in greater levels of extractables. The abovementioned advantages of metallocene catalysed polymer are in addition to other benefits that arise from the use of metallocene catalysed, such as super-random distribution of comonomers and controlled and variable MWD.

Improved Ethylene-based Polymer Blends

One aspect of the present invention relates to improved blends of one-or-more ethylene-based polymers and/or copolymers and, optionally, one or more higher (C_3 - C_{20}) α -olefin polymers and copolymers which are suitable for the production of injection moulded flexible thin walled mouldings. A two-or-more ethylene-based polymer blend consist of an at-least-one ethylene-based polymer, usually the bulk polymer, and one or more ethylene-based miscible polymers.

An at-least-one ethylene-based ALOP is a polyethylene or ethylene/ α -olefin copolymer or ethylene copolymer copolymerised with copolymers containing functional groups such as acetate, acrylate, methacrylate etc. Preferably the ethylene-based ALOP is a polyethylene or ethylene/ C_3 - C_{20} α -olefin copolymer. More preferably the ALOP has an MFI (measured as I_2) >10 , preferably >20 more preferably >30 and most preferably >50 . Preferably the ALOP has a density $<0.913\text{g/cm}^3$, more preferably a density $<0.90\text{g/cm}^3$ and most preferably a density $<0.89\text{g/cm}^3$. Most preferably the ALOP is made using a metallocene or similar catalyst capable of producing polymers characterised by super-random distribution of the copolymers between and within the molecular chains of the ALOP.

The one-or-more ethylene-based miscible polymer is either a polyethylene or ethylene/ C_3 - C_{20} α -olefin copolymer or ethylene/ α -olefin copolymer copolymerised with copolymers containing functional groups such as acetate, acrylate, methacrylate etc., more preferably a polyethylene or ethylene/ C_3 - C_{20} α -olefin copolymer having an MFI >10 , preferably >20 , more preferably >30 and most preferably >50 . More preferably the one or more ethylene-based miscible polymer is either a polyethylene or ethylene/ C_3 - C_{20} α -olefin copolymer having a crystallinity greater than the density of the ALOP with which it is blended. The crystallinity difference is preferably $>5\%$, more preferably $>10\%$. Even more preferably the one or more ethylene-based miscible polymer is characterised by having a branched (i.e. non-linear) structure and melting points, crystallinities and MFIs greater than those of the ALOP in the blend, and is made using a metallocene or similar catalyst and/or a Z-N or similar catalyst or a high-pressure/free radical reactor process.

The ALOCAs of the present invention is advantageously a polypropylene homo and/or copolymer. Suitable polypropylene-based ALOCAs include isotactic, syndiotactic and atactic polypropylene of various MFIs, densities and crystallinities as would produce desired injection moulded flexible thin walled mouldings. Particularly when blended with ALOPs containing low molecular weight plastomers and/or substantially linear polyethylenes, a wide variety of polypropylene polymers possessing a very wide range of MFIs, densities and crystallinities will

produce blends suitable for use in the manufacture of injection moulded flexible thin walled mouldings. The propylene-based ALOCAs may be propylene homopolymers, block or random copolymers with various α -olefin copolymers, preferably copolymers of propylene with ethylene or butene in which the ethylene or butene component constitutes less than 35% of the polymer. It is further advantageous that the propylene-based ALOCA has a crystallinity that is greater than the overall crystallinity of the ALOP phase of the composition. The propylene-based polymer used as the ALOCA may be manufactured using a variety of catalysts, including metallocene catalysts.

Preferably the propylene based polymer will have a MWD of from 1.8 to 4.0 and a narrow composition distribution that is characteristic of metallocene or similar catalysed propylene polymers. However, propylene based polymers such as are cited in US 6,476,173 and which have MWDs up to 20 will often produce good results. Random ethylene/propylene/vinyl aromatic interpolymers such as ethylene/propylene/styrene interpolymers may also be used as the ALOCA in the present invention.

In general, the ESCR of a particular ALOP/ALOCA blend increases as the percentage of the α -olefin content of the polypropylene-based ALOCA component of the composition increases. Thus for a given percentage of a composition, a propylene/ α -olefin copolymer will usually impart a higher ESCR to a particular ALOP/ALOCA composition than will the same percentage of propylene homopolymer with the same MFI.

Improved Polypropylene ALOP Polymer Blends

A further aspect of this present invention relates to compounds for the manufacture of flexible thin walled compounds that are characterised by having PP and copolymers thereof as the ALOPs of the blends.

In recent times a number of advances in PP polymerisation—and particularly in catalyst developments—now make the successful development of an improved range of cost and performance-effective polypropylene-based compounds possible. In particular, the ability to 'tailor' PP homo and copolymer molecules to have specific properties have resulted in the polymerisation of polypropylene homo and copolymers that can be used 'as is', i.e. that don't necessarily require compounding with other polymers to have utility for tube production. Developments of particular interest in this regard are the ability to make elastomeric PP homo polymers by altering the tacticity of the polymer by various means as well as the ability to produce low flex modulus PP α -olefin copolymers with relatively low percentages of α -olefin copolymers. Some of these developments are described above under the heading "New Materials for Use in Injection moulded flexible thin walled mouldings".

When the ALOP of a blend is a linear, substantially linear or branched polymer in which propylene or butene constitutes over 50% of the polymer, the MFI of the ALOP homo or α -olefin copolymer may be higher than is generally acceptable when ethylene α -olefins constitute the ALOP due to propylene and butene homo or α -olefins generally possessing better inherent ESCR properties at the same MFI compared to most ethylene α -olefins. Thus some propylene and butene homo or α -olefin copolymers, particularly those prepared by metallocene or similar catalysts, can have MFIs up to and greater than 150 and still produce acceptable injection moulded flexible thin walled mouldings with good ESCR when used as the ALOP. The optimum MFI for a particular propylene or butene homo or α -olefin copolymer ALOP can be determined by experimentation, but will preferably be >30, more preferably >50 and, depending on the characteristics of the particular polypropylene or polybutene homo or α -olefin copolymer, may be even more preferably >100 and most preferably >150. α -olefins suitable for copolymerisation with propylene or butene to produce propylene or butene α -olefins

suitable for injection moulded flexible thin walled mouldings include α -olefins in the range of about 2 to about 20 carbon atoms, preferably in the range of about 2-16 carbons, most preferably in the range of about 2-8 carbon atoms. A more detailed description of suitable α -olefin co- and ter-polymers may be found in the relevant sections of the '255 patent. Further, the copolymer may contain as a comonomer 0.5 to 10% by weight of a nonconjugated diene, such as 1,4-hexadiene, 5-methyl-1,5-hexadiene, 1,4-octadiene, cyclohexadiene, cyclooctadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-butyldiene-2-norbornene, or 2-isopropenyl-5-norbornene. Preferably these copolymers are prepared using metallocene or similar catalysts. The percentages of ethylene and/or other α -olefins copolymerised with propylene or butene to form polymers suitable for injection moulded flexible thin walled mouldings can be varied widely, depending on the desired properties of the mouldings made from blends of these materials. In general, the higher the percentage of ethylene and/or other α -olefin copolymer polymerised with the propylene or butene, the lower the flex modulus of the resultant polymer and so the more flexible the mouldings made from them will be in which said polymers constitute the ALOP of the blend.

Blends designed for recoverability and which contain a dispersed phase of a greater crystallinity and a continuous phase of lesser crystallinity such as are described below are suitable for the production of injection moulded flexible thin walled mouldings. The sizes of the individual domains of the dispersed phase in these blends are preferably very small. The components of the blend are also compatible to the extent that no compatibiliser needs to be added to attain and retain this fine morphology. One of the components is a polymer comprising predominately stereospecific polypropylene, preferably isotactic polypropylene (an XPP). This is the component with greater crystallinity. A second component is a copolymer of propylene and at least one C_2 , C_4 - C_{20} α -olefin, preferably ethylene. This is the component with lesser crystallinity (an SXPP). In the copolymer the propylene is preferably polymerised substantially stereospecifically. Preferably the copolymer has a substantially uniform composition distribution, preferably as a result of polymerisation with a metallocene catalyst. Most preferably, said XPP is an ethylene propylene copolymer, e.g. ethylene propylene semicrystalline elastomer.

It has been found that blending an at-least-one XPP and an at-least-one SXPP results in advantageous processing characteristics while still providing a composition having decreased flexural modulus and increased tensile strength, elongation, recovery and overall toughness. A third polymeric component which is another crystallizable propylene α -olefin copolymer (an SXPP2) has a crystallinity between those of the XPP and SXPP. One type of PP blend suitable for injection moulded flexible thin walled mouldings comprises a crystalline isotactic or syndiotactic polypropylene (XPP) with a semi-crystalline α -olefin PP copolymer (SXPP) of the same tacticity as the XPP, preferably an ethylene propylene copolymer containing 4 wt. % to 35 wt. % α -olefin, preferably ethylene, and optionally a second propylene α -olefin copolymer with a crystallinity intermediate between the XPP and SXPP and with similar tacticity. These blends have heterophase morphology. It is believed that this matching of stereoregularity increases the compatibility of the components and results in improved adhesion at the interface of the domains of the polymers of different crystallinities in the polymer blend composition. Narrow intermolecular and intramolecular compositional distribution in the copolymer is preferred, but not essential. These and similar blends may be particularly suitable for the manufacture of flexible injection moulded flexible thin walled mouldings and other containers that are subjected to heating by such methods as heat-filling with the product the container is required to contain and/or heat treating the filled container by methods such as retorting. Blend composition can vary widely depending on the application and may comprise 1% to 95% by weight of XPP and a SXPP with greater than 65 percent by weight propylene and preferably greater than 80% by weight propylene.

Polypropylene-based ALOP compositions that have low flex modulus have particular utility for injection moulded flexible thin walled mouldings. The following are illustrations of some broad formulations that are capable of providing suitable low-flex-modulus PP compositions.

Formulation Type 1

1. 8-25% crystalline PP or PP copolymer, most preferably 12-18%. If it is a copolymer, it should have at least 85% by weight of PP, preferably more than 90%.
2. 75%-92%, most preferably 82-88%, of two elastomeric polymers, Polymer a) and Polymer b): Polymer a) having 15-32% α -olefin, preferably 25-30%, optionally including 0.5-5% diene and Polymer b) having 32-45% α -olefin, preferably 35-40%, optionally including 0.5-5% diene. The weight ratio of polymer a) to polymer b) is 1:5 to 5:1.

The above composition may be prepared by sequential polymerisation or blending. The preferred α -olefin is ethylene. Depending on properties needed, the above compositions may be used in combination with EPR (ethylene/propylene copolymers), ethylene/propylene/diene terpolymers (EPDM), ethylene/ C_4 - C_{12} α -olefins (eg. ethylene/octane such as Engage). Such elastomeric polymers may be present in 5%-80% weight of composition.

Formula Type 2:

- 1) 10-60 % of a crystalline propylene homo or co polymer
- 2) 10-40 % propylene/ethylene copolymer insoluble in xylene (i.e. low ethylene copolymer content) and
- 3) 30-60% ethylene/propylene copolymer soluble in xylene at room temp (i.e. high ethylene copolymer content)

The above composition may be prepared by sequential polymerisation or blending.

Formula Type 3 :

- 1) 70-98% of a crystalline PP homo or copolymer
- 2) 2-30% somewhat xylene insoluble propylene/ethylene copolymer (i.e. relatively low ethylene copolymer)

This blend has a relatively high flex mod, due to the relatively high % crystalline copolymer and relatively low α -olefin PP copolymer, and may be prepared by sequential polymerisation or blending.

Other types of formulations include simple blending of a variety of different types of PP ALOPs such as have been mentioned above, preferably PP homo polymers of different tacticities and PP α -olefin copolymers of various tacticities and degrees of α -olefin content together with ALOCAs of various types, particularly mPEs and PP homo polymers of different tacticities and PP α -olefin copolymers of various tacticities and degrees of α -olefin content having a lower flex modulus than the PP ALOP used in the particular blend.

In addition to its use in PP blends, blends of HD/MD/LDPE with PE copolymers that can act as 'tie molecules', eg. low density mPE, can also be improved using the techniques of spherulite boundary strengthening. This enables the tie molecules to be concentrated at the crystal boundary, which effectively increases the number of tie molecules at the crystal interface, which in turn leads to increased blend ESCR.

High-MFI-ALOCA Blends

In a further development of the present invention, we have found that the ALOCAs of polymer blends, particularly blends in which polyethylene, polypropylene or polyesters such as PET constitute the ALOCA may advantageously be replaced by one or more ALOHMFCAs. Preferred ALOHMFCAs are ethylene, propylene or butene homo or α -olefin interpolymers, preferably produced using a metallocene or similar catalyst. ALOHMFCAs may also be terpolymers, such as one comprising ethylene propylene or butene, an additional and different α -olefin to the first α -olefin and a diene, preferably a diene containing 7 to 10 carbon atoms, and having an amount of diene effective to cause an increase in MFI compared to corresponding linear copolymer without diene. Polymers conforming to the above description are described in US 6,509,431, and depending on their MFI and other characteristics, may also be used as ALOPs or ALOCAs.

As an example of this further development we found that direct replacement of a 100 MFI PP with a 350 MFI PP in PE ALOP/PP ALOCA blends resulted in:

1. Improved flow of the compound
2. Improved ESCR
3. Improved clarity of the moulding
4. Better 'feel', i.e. a softer moulding
5. Better compatibility/stability of the blend components.

Some of the above improvements are no doubt the result of the decrease in interfacial tension between a PP and the ALOP (i.e. the mPE/LDPE) that occurs with decreasing MW of the PP, which in turn results in improved compatibility/stability of such blends. It is also worth noting that the interfacial tension between the PP and the PE components, particularly the metallocene PE component, decreases with increasing comonomer content of the mPE. Also, at a given percentage of comonomer in the mPE, the higher the chain length of the comonomer the lower the interfacial tension; eg. octene copolymers produce a lower interfacial tension than the equivalent butene copolymer. All of these factors contribute to the abovementioned improvements. The improved blend stability that frequently results from the use of ALOHMFCAs often has the additional effect of enabling the production of finer dispersions (i.e. smaller particle size) of the ALOHMFCA within ALOP. This in turn often results in improved large strain properties (such as ESCR) of the compositions as well as the improved clarity of the mouldings.

In general, and provided that the ALOHMFCA largely forms the disperse phase of a blend, the MFI of the ALOHMFCA doesn't significantly affect the ESCR of the composition. Thus one can obtain the benefits of increasing the overall MFI of compositions of the present invention through the incorporation of ALOHMFCAs into blends without causing significant degradation of the compound's ESCR.

We have also found that provided the molecular weight of the ALOHMFCA doesn't fall below a value beyond which its ability to improve or maintain the blend ESCR and/or tear strength in the direction of the polymer flow of the moulded blend is seriously negated, the incorporation of ALOHMFCAs into the blend has a number of significant advantages relative to the incorporation of low MFI (<100) grades of the same polymer. For example, the ALOHMFCA frequently has the effect of increasing the shear sensitivity and overall MFI of the whole blend, thereby improving its flow properties and making it possible to mould larger/longer injection moulded flexible thin walled mouldings. Also, because there is usually an inverse relationship between MFI and some physical properties of polymers, it is frequently found that polymer properties such as flex modulus and hardness decrease with increasing MFI. When it is

desired, for example for reasons of cost, ESCR effectiveness, etc., to use as a particular ALOCA but the low MFI grades of that polymer (i.e. polymers with MFIs ≤ 100) have a flex modulus that is too high relative to the desired application which results in mouldings and that are too stiff, the substitution of a high MFI (>100) chemically similar or identical ALOHMFCA for all or part of the ALOCA in a blend enables the production and use of blends with much higher MFI while at the same time reducing the flex modulus of the moulding. Depending on the desired properties of the moulded article, the ALOHMFCA can be used either on its own in a blend or may be blended with ALOCAs.

Replacing all or part of an ALOCA with the same weight % of a chemically equivalent ALOHMFCA in a blend and compounding said blend most often results in a significant increase in the number of particles of the chemical within the blend, which in turn results in a significant increase in the number of nucleation sites for the ALOP. This in turn leads to smaller crystals of ALOP being formed, which in turn frequently leads to an increase in blend ESCR, clarity, tear strength, etc. Without wishing to be bound by theory, it is believed that the interaction between the ALOP and ALOCA and/or an ALOHMFCA forms regions within the moulded articles which can be regarded as "joints". These "joints" appear to absorb or disperse stresses in articles made from the polymer blend. The presence of these "joints" interspersed within the article appears to absorb or dissipate the stresses within the article which would otherwise result in decreased physical properties. We believe that the benefits obtained from the use of an ALOHMFCA are due primarily to their being more effectively dispersed in the ALOP relative to lower MFI versions of the same ALOP and that they enable the formation of more and smaller disperse phase particles. In general, the higher the MFI of the ALOHMFCA, the smaller the particle size that it can form, although there will be an MFI (and hence MW) beyond which reducing the MW further will not result in further significant reductions in ALOHMFCA particle size. In addition, the smaller particle size of the disperse phase in turn results in an increase of the total surface area of a given weight percentage of the ALOCA/ALOHMFCA, thereby increasing the areas of interaction between the ALOP and the disperse phase of the blend. The effect of reducing the particle size of an ALOCA/ALOHMFCA on the number of particles of the ALOCA/ALOHMFCA in the blend is illustrated by the fact that for a given weight % of an ALOCA/ALOHMFCA in a blend, halving the particle size (eg. by halving the particle radius) increases the number of ALOCA/ALOHMFCA particles by a factor of 8 and the total surface area of the ALOCA/ALOHMFCA by a factor of 2. Thus halving the radius of the particles of ALOCA/ALOHMFCA increases the number of stress-relieving 'joints' within the moulding by a factor of 8 and the surface area of the interface between the ALOCA/ALOHMFCA and the ALOP by a factor of 2. Both these increases have the potential effect of improving properties such as ESCR and tear strength.

Again without wishing to be bound by theory, we believe that the increase in particle numbers and surface area of the ALOHMFCA is one of the key reasons for many of the property improvements (eg, ESCR, tear strength, clarity) of the present invention. The improvements in ESCR etc. resulting from the incorporation of high MFI compatible polymers often enables the percentages of ALOCA/ALOHMFCA in a blend to be reduced while still attaining an acceptable ESCR etc. This may be advantageous, for example where it is desirable to reduce the amount of a PP ALOCA in a blend in order to reduce its flex modulus. Alternatively, and using the same example, maintaining the weight % of the ALOHMFCA PP results in significant increase in the number of disperse phase particles relative to a low MFI equivalent PP which in turn increases the overall ESCR of the blend. This ESCR improvement in turn enables the use of higher MFI ALOPs (i.e. ALOPs with inherently lower ESCR), thereby increasing the blend's processing characteristics while maintaining acceptable ESCR performance.

High MFI polypropylenes suitable as an ALOHMFCA for use in the process of the present invention include isotactic, syndiotactic and atactic polypropylene and blends thereof of various MFIs, densities and crystallinities as would produce desired properties in products moulded by the process of the present invention. Polypropylenes particularly useful as ALOHMFCAs in the present invention are homopolymers or copolymers of propylene and one or more α -olefins selected from ethylene or linear or branched C_4 to C_{20} α -olefins, preferably ethylene or C_4 to C_8 α -olefins, preferably ethylene or 1-butene or hexene or octene, and optionally, minor amounts of non-conjugated diolefins, preferably C_6 - C_{20} diolefins. In one embodiment. The α -olefin can contain cyclic structures that are fully saturated such that the α -olefin monomer does not contain a cyclic moiety with any olefinic unsaturation or any aromatic structures. Other cyclic structures may contain various degrees of unsaturation.

Blends of the present invention incorporating ALOHMFCAs generally comprise in the range of about 40 to about 99.9 weight percent of the ALOP, and preferably 60 to about 0.1% of an ALOCA, of which all or part is an ALOHMFCA. These are preferred ranges. The particular ALOP component, the particular ALOHMFCA and the relative amounts of each used in G3 blends will depend on the requirements of the particular application for which the blend will be utilized, economics, and other process factors and can be determined by experimentation.

The ALOHMFCA is used in an amount at least sufficient to improve the environmental stress crack resistance and/or tear resistance, as measured by the Gullwing tear test, of the polymer blend. The ALOHMFCA may also be used in amounts in excess of those required to compatibilise the polymer blend in order to improve the viscosity characteristics of said polymer blend so as to optimise the moulding characteristics of said polymer blend and/or general properties of the moulded product such as softness and flexibility. Typically, the ALOHMFCA is used in an amount of from about 2 to about 60 weight percent of the polymer blend, although lower amounts may be used in certain polymer blends. Additionally, compatibilisers that improve various properties of the blends—such as weld line strength, compatibility between the ALOP and ALOHMFCA/ALOCA, disperse phase particle size reduction, ESCR, tear strength, etc.—may advantageously be added to the blends. The abovementioned and other suitable additives may be added to one or more components of the polymer blend or the polymer blend as a whole prior to moulding in order to modify its properties to suit specific applications or to achieve specific effects in the end product.

Although PP homo and copolymers are generally particularly effective ALOHMFCAs, a high MFI (>100) version of virtually any ALOCA may be suitable for use as an ALOHMFCA in blends of the present invention. One or more of the polymer components of either or both the ALOP or the ALOHMFCA may advantageously be produced with a metallocene or similar catalyst system, and may have a narrow or broad molecular weight distribution.

Also included as suitable ALOHMFCAs are blends of polymers, such as a neutralised ionomer such as a Surlyn (Dupont) and EEA and/or EMA and/or EMAA. For example, a low MFI partly neutralised ionomer such as Surlyn 9970 (MFI = 14) may be compounded with a high MFI EMA such as Nucrel 599 (Dupont) (MFI = 500) to achieve an ALOHMCA blend with a higher MFI than is achievable with the Surlyn alone, while still being able to benefit from the beneficial properties of the Surlyn.

Alkyl carboxyl substituted polyolefins suitable as ALOHMFCAs may include substituted polyolefins where the carboxyl groups are derived from acids, esters, anhydrides and salts thereof. Carboxylic salts include neutralised carboxylic acids and are often referred to as ionomers (eg. Surlyn). Typically acids, anhydrides and esters include methacrylic acid, acrylic acid, ethacrylic acid, glycidyl maleate, 2-hydroxyacrylate, diethyl maleate, maleic anhydride, maleic acid, esters of dicarboxylic acids, etc. Preferred examples include ethylenically

unsaturated carboxylic acid copolymers such as polyethylene methacrylic acid and polyethylene acrylic acid and salts thereof. Copolymers of anhydrides of organic acids include copolymers of maleic anhydride as well as copolymers of cyclic anhydrides.

Non-PE or PP ALOP blends

In a further development of the present invention we have developed blends suitable for the production of flexible thin walled mouldings that are characterised by having ALOPs that are neither PE or PP polymers. Thus blends of the present invention include blends in which polyesters such as PET, PEN, PBT and polyamides such as various nylons are the ALOPs.

Because the ALOPs of these blends have inherently better barrier (eg. oxygen transmission rate) properties than blends using polyethylene or polypropylene as the ALOP, such blends are particularly suitable for the production of injection moulded flexible thin walled mouldings with improved barrier properties. However, the problem with 'pure' PET, PEN, PBT, Nylon, etc. is that they are too stiff at typical tube wall thicknesses and consequently produce injection moulded flexible thin walled mouldings that are unsuitable for commercial use. These new compounds are effectively blends of 'barrier' ALOP polymers such as PET with one or more ALOCAs or ALOHMFCAs together with, if appropriate, plasticisers (eg. N-Butylbenzene sulfonamide (BBSA)) or compatibilisers capable of compatibilising the ALOP with the ALOCA or ALOHMFCAs, that in combination act to reduce the flex modulus of the blend relative to that of the ALOP. Blends of the present invention are designed to reduce the inherent 'stiffness' of PET, etc., thereby enabling these materials to be used for tube production while still maintaining the high barrier ALOP as the continuous phase of the blend.

Using a particular PET blend as an example of this further development of the present invention, the blend can consist of a high MFI PET polymer, a low flex modulus ALOCA or ALOHMFCA such as a low density mPE or butadiene-containing PE or PP or low flex modulus PP homo or copolymer or functionalised low density mPE or low flex modulus PP homo or copolymer and optionally a compatibiliser such as a glycidyl-group-containing PE or PP blended in such proportions that the PET component forms the continuous phase of the blend with the mPE or PP homo or copolymer forming the discontinuous phase. Because the PET is the continuous phase, injection moulded flexible thin walled mouldings made with such a blend will effectively present a relatively high barrier polymer to both the contents of the tube and the exterior, while the disperse phase mPE will act to reduce the overall flex modulus of the tube. As an example, such a blend could consist of between 35 and 95% polyalkylene terephthalate (eg. PET, PBT, PEN) and about 1 to about 50 weight percent of a polyethylene or other polyolefin, and from about 5 to about 15 weight percent of a compatibiliser, such as a glycidyl group-containing copolymer compatibiliser. More preferably, the compositions comprise between about 50 and about 65 weight % of polyalkylene terephthalate, between about 20 and about 40 weight % of polyethylene and between about 8 and about 12 weight % of the third compatibiliser component. Advantages of these types of compositions are that the continuous phase of the material is that which has the best barrier properties and therefore presents the best barrier to oxygen and the tube contents, but has a disperse phase that can be very soft, leading to a softer pack than would be the case if it was made out of the high barrier material alone. It will be understood by those skilled in the art that a variety of compatibilisers, ALOCAs or ALOHMFCAs and barrier ALOPs can be used to produce blends of the present invention. An alternative compatibiliser component includes an isocyanate functional group-containing copolymer of alpha-olefin.

Nanocomposite Blends

In yet a further variation of the present invention, blends containing nanocomposites and/or relatively high levels of other ACAs capable of nucleating the ALOPs or ALOCAs of the

blend. Usefully, the nanoparticles of these blends are clays, most frequently organo-clays. These blends are particularly useful for the production of injection moulded flexible thin walled mouldings with significantly improved barrier properties relative to the same compound without the nanoparticles. The incorporation of nano-sized particles into blends also has the benefit of improving the ESCR of the compound relative to the same compound without the nano-sized particles, which in turn significantly enlarges the blend formulation window.

We have found that the addition of fine, ultra-fine and/or nano-sized particles for the production of injection moulded flexible thin walled mouldings frequently leads to improved properties of the injection moulded flexible thin walled mouldings. Such blends may contain fine, ultra-fine or nanoparticle-sized polymers or clays or metal oxides such as ultra-fine barium sulphate (which may have a particle size of 10nm), particles of other inorganic metal oxides such as those of zinc, electrically conductive tin, e.g., antimony containing tin oxide, iron, zirconium, aluminium, chromium, yttrium, europium, mixtures thereof, among others. Fine, ultra-fine and nano-sized particles may be powders having a primary crystallite size of from about 1 to 200 nm, preferably <100nm and often from about 4 to about 60 nm. These crystallites can form agglomerates with an average size up to about 300 nm. Also included in the definition of nanocomposites are blends containing non-clay crystallising/nucleating agents capable of crystallising/nucleating the ALOP(s) and/or ALOCA(s) of the blend. Although for 'normal' mouldings nucleating agents are often added in quantities at 0.1% or less, for the present invention it is preferable to add crystallising/nucleating agents in quantities greater than 0.1 weight percent, preferably >0.3%, more preferably >0.5% and sometimes >1%. The optimum amount added to a particular blend may be determined by experimentation. There are many non-clay crystallising/nucleating agents, such as metal salts of organic acids such as sodium and lithium benzoates, sorbitol derivatives, glycol derivatives, etc. and are well known to those skilled in the art.

Nanoparticles, preferably those with very high aspect ratios and particularly—but not exclusively—those consisting of modified clay minerals, can advantageously be used as an ACA for the manufacture of injection moulded flexible thin walled mouldings. In addition to enhancing the barrier properties of containers, nanoparticles can also enhance the heat stability and mechanical properties of thin walled flexible articles such as containers. An increased heat stability for a container is important in order to allow for "hot-filling" applications. "Hot filling" applications allow for aseptic uses of containers in the food processing industry and also extend the shelf life of various food products.

When the nanoparticle is a clay, organo-clay or other particle of nano-proportions with a high aspect ratio, even small weight percentages of the nanoparticles relative to the polymer material provide increases in the ESCR, impermeability and other physical properties of flexible thin walled articles. As a guide, the higher the average aspect ratio of the nanoparticle and the greater its average diameter, the greater the improvement in barrier properties that the particles will confer on the nanocomposite. For example, a nanocomposite in which the nanoparticles have an average aspect ratio of 1000 will have better barrier properties than a nanocomposite with the same weight percentage and chemical type of nanoparticles but with an aspect ratio of 100. Conversely, and using the above example, the nanocomposite in which the nanoparticles have an average aspect ratio of 100 will frequently have an inherently better ESCR than the nanocomposite with the 1000 aspect ratio nanoparticles because there will be a greater number of individual particles in the former nanocomposite, which in turn will result in a greater number of nucleation sites for the polymers, hence a greater number of polymer crystals will be formed, which in turn will result in an inherently better ESCR. When the nanoparticle is a particle that does not have a specially high aspect ratio, such as nano-sized TiO_2 , other metal oxides, etc., even small weight percentages of the nanoparticles relative to the polymer material provide increases in the ESCR and other physical properties of flexible thin walled articles, but

the barrier properties of such nanocomposites will not be as good as a nanocomposite in which the nanoparticle has a high aspect ratio. Typical non-fine TiO_2 such as are extensively used in the plastics industry, such as Dupont TiO_2 grades for plastic applications have a mean particle size of 350nm (Grade R960) and 220nm (Grade R104), and so do not fall within the scope of blends of the present invention.

Nanoparticle/polymer blends for injection moulded flexible thin walled mouldings may be fabricated through various methods. One such method is compounding wherein the ingredients are intimately melt-mixed together into as nearly a homogeneous mass as is possible. Other methods of integrating the polymer layer in between the clay/organo-clay platelet include in situ polymerisation, solution intercalation and melt exfoliation. The organo-clays preferred for tube production differ from ordinary untreated clays in the fact that the untreated clays typically form only ordinary phase-separated mixtures when blended or mixed with a polymer. The clays which are organically modified are more easily dispersed in the polymer matrix and can form a nanocomposite of two types: i.e. mainly intercalated or mainly exfoliated structures. In order to obtain better compatibility between the polymer—and particularly polyolefin polymers—and the organo-clay it is often desirable that the organo-clay contains substituted alkyl side chains. Blends particularly suitable for tube production comprise between about 0.01 and about 25 wt %, preferably between 0.5 and 25 wt %, more preferably between 0.5 and 15 wt % and most preferably between 0.5 and 10 wt % of at least one expanded organo-clay

The organo-clays suitable for tube production generally have a particle size from about 1 to about 10,000 nanometres, desirably from about 100 to about 2,000 nanometres, and preferably from about 200 to about 500 or 1,000 nanometres. When the main polymer to be used to form the nanocomposite and/or nanocomposite master-batch (i.e. a concentrate for subsequent dispersion in another polymer) is a polyolefin, it has been found that, all other things being equal, the greater the degree of short-chain branching in the polymer (as measured by SCBI) the greater the extent of exfoliation of the organo-clay, and hence the better the overall properties of the nanocomposite. In the case of olefin/ α -olefin and other copolymers, the greater the percentage of α -olefin or other copolymer in the polymer the greater the extent of exfoliation of the nanocomposite. Also, polymers exhibiting super-random distribution of the monomers within the polymer molecules are particularly suited to the production of nanocomposites of the present invention as their use tends to give greater degrees of exfoliation than similar polymers not exhibiting super-random distribution of the monomers. Such super-random polymers may be catalysed by metallocene or similar catalysts which are well known in the art.

Particularly advantageous are blends in which the fine, ultra-fine or nanoparticle-sized particles have the following characteristics:

- 1) Average particle size between 0.9 and 100nm and an aspect ratio of between 100 and 2000.
- 2) Preferably has a thickness of $<2\text{nm}$ and a diameter between 10 and 1000nm.

Typically, clays of various types such as the following are preferred ACAs which may have the above characteristics. Preferred swellable layered clay materials are phyllosilicates of the 2:1 type having a cation exchange capacity of 50 to 200 milliequivalents per 100 grams of mineral. The most preferred swellable layered clay materials are smectite clay minerals such as montmorillonite. Other non-clay materials having the above described ion exchange capacity and size, such as chalcogens may also be used as the source of platelet particles for polymer blends for tube production.

To maximise the degree of exfoliation of any intercalated but not exfoliated galleries of the clay/organo-clay it is advantageous that the compound be subjected to very high shear rates

during the moulding process. This can be achieved by filling the cavity forming the tube at a very fast rate. We use the 'Standardised Fill Ratio' as a measure of fill rate. The 'Standardised Fill Ratio' is, when expressed in units of mm/sec, preferably >250, more preferably >300, yet more preferably >400, even more preferably >500, yet even more preferably >700, particularly preferably >800 and most preferably >1000. The 'Standardised Fill Ratio' is calculated by the following formula:

$$\text{Standardised Fill ratio (mm/sec)} = \text{flow length (in mm)} / \text{Fill time (sec)}$$

where 'Standardised Fill Ratio' is the average rate (in mm/sec) at which the polymer flows into a cavity forming the tube during the injection process, 'flow length' is the measurement of the longest polymer flow path from the injection gate(s) of the cavity to the point of the moulding furthest from said gates and 'Fill time' is the time required to fill the cavity with polymer and is measured from the commencement of the injection of the polymer into the cavity until the cavity is filled with polymer and the 'hold' time commences.

Clays naturally tend to exist as 'tactoids' or 'galleries', which are an agglomeration of up to and sometimes greater than 100 individual clay platelets. In order to achieve the maximum benefit from the nanocomposites, and particularly clay nanocomposites, the individual nanoparticles need to be evenly dispersed throughout the polymer matrix. In the case of clays, the process of separating the individual clay platelets is called exfoliation. Exfoliation may be achieved in a number of ways, but the most commonly used method is to introduce an appropriate intercalant into the galleries of the clay and then apply shear to separate the individual platelets. The intercalant also should preferably have a functional group that can interact with the polymer and effectively link the platelets to the polymer. An epoxy resin such as bisphenol A can be used as an intercalant.

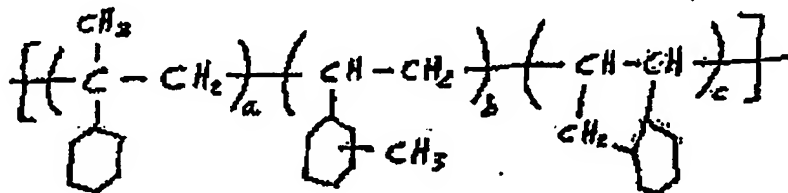
There are a number of intercalants suitable for the production of nanocomposites for tube production. Particularly useful are intercalants comprising an organic compound having a non-polar portion bonded to a polar portion. The non-polar portion may, for example, be a saturated oligomer of isoprene which tends to be compatible with non-polar polymers, especially copolymers of both propylene and ethylene. The polar portion tends to have an affinity for the silicate platelets of the clay material. Consequently, the organic compound enhances the compatibility of the intercalated clay materials that, when melt blending with sufficient shear to exfoliate the intercalated clay material, results in the exfoliation of intercalated clay into the polymer.

There are a number of ways in which nanocomposites can be prepared and which are described in the literature. Some of the methods that may be particularly suited to the production of nanocomposites suitable for tube production are highlighted below. Of particular interest for the production of injection moulded flexible thin walled mouldings are nanocomposites in which the bulk polymer is a polyolefin such as polyethylene or polypropylene or a polyester such as PET or PEN, said polymers being particularly suited, by reason of cost and other polymer properties, for the production of injection moulded flexible thin walled mouldings. As is well known, forming nanocomposites with polyolefins presents special challenges due to the essentially non-polar nature of said polymers and the consequent difficulties in achieving significant degrees of exfoliation of the organo-clay. However, the development of new intercalants and methods of achieving such nanocomposites have resulted in improvements in the performance and manufacture of polyolefin-clay nanocomposites. These developments, together with the exceptionally high shear rates generated during the injection moulded tube process which facilitate the exfoliation of non-exfoliated clays, can produce polyolefin nanocomposites that have good barrier and other beneficial properties.

One of the ways of improving the degree of exfoliation of organo-clays in polyolefins is through the addition and compounding together of a modified polyolefin—such as a maleic

anhydride modified polyolefin polymer or oligomer—and an organic cation such as a quaternary ammonium exchanged multi-layered clay. This process results in a masterbatch which is then added to and compounded with a suitable polyolefin. The organo-clay thus produced has sufficient polarity to enable significant exfoliation of the clay when subjected to the shear stress during compounding with the polyolefin, and particularly during the high shear manufacturing process to produce injection moulded flexible thin walled mouldings.

Another approach is to incorporate a hydrogenated C₉ aromatic polymer that is compatible with both the polyolefin bulk polymer of a blend and a cation exchanging layered silicate material such as clay and compounding the resultant mix at an appropriate temperature. Generally the hydrogenated C₉ aromatic polymer and the cation exchanging layered silicate material are added in roughly equal amounts. Preferably the cation exchanging silicate material is washed in water to remove impurities, and may advantageously be subsequently treated with a suitable quaternary cation such as a quaternary ammonium cation. An example of a suitable hydrogenated C₉ aromatic polymer is a polymer with the following formula:



Polymers conforming to the above formula are available from Arakawa Chemical Industries under the trade name ARKON. Other cyclic polymers containing unsaturated bonds, either within the cyclic group or in the polymer chain itself, will be suitable for the production of polyolefin organo-clay nanocomposites and may be determined by experimentation. One advantage of polymer/organo-clays manufactured using cyclic groups is that because they preferably have cyclic groups within them, they may well be particularly suitable as oxygen scavengers, particularly when compounded with catalysts capable of catalysing the oxidation of the cyclic and/or unsaturated functional groups. It is known that many oxygen scavengers containing cyclic groups produce fewer by-products than linear oxygen scavengers and which can migrate and thereby contaminate products packed into containers incorporating said oxygen scavengers. In such cases the polymer/organo-clay will perform the dual functions of a nanocomposite and oxygen scavenger.

Another method for preparing organo-clays capable of incorporation into polyolefins is to first functionalise the nanofiller with an aminosilane. Thereafter, a carboxylated or maleated polyolefin is grafted to the filler through an amine-carboxyl reaction. The resulting modified filler is dispersed in a semi-crystalline polyolefin (eg. polyethylene or polypropylene). Co-crystallization between the carboxylated or maleated polyolefin and the semi-crystalline polyolefin can improve interaction between the filler and semi-crystalline polyolefin.

Yet another method of preparing a polyolefin-compatible nanocomposite is to prepare an organophilic clay that is dispersible in non-polar organic solvents. The organophilic clay can then be treated with an alkyl aluminoxane and subsequently a catalyst, including Ziegler-Natta and metallocene catalysts, to form a complex that promotes olefin or styrenic polymerisation and platelet dispersion. The nanocomposite can be prepared directly by in situ polymerization of the olefin or the styrene at the nanofiller particles without shear, without an ion exchange step, and without the need to incorporate polar substituents into the polyolefin or polystyrene.

Another nanocomposite suitable for injection moulded flexible thin walled mouldings consists of a non-polar bulk polymer such as polyethylene or polypropylene, an intercalated cation exchanging multi-layered silicate material such as an acid or quaternary ammonium treated montmorillonite or sepiolite clay, dispersed in the bulk polymer and an organic cation, such as polyethylene or polypropylene terminated by an amine group, the organic cation having a pendent polymer chain, the polymer of the pendent polymer chain being miscible with the bulk polymer. The nanocomposite material is made by blending the molten bulk polymer with the cation exchanging multi-layered silicate material and the organic cation.

It is well known that different intercalants result in different degrees of exfoliation; for example, octadecyl amine onium clay intercalant produces significantly better nylon-based nanocomposite barrier films compared to the same polymer nanocomposite in which the clay intercalant is an n-alkyl dimethyl benzyl amine onium ion

Yet another beneficial and interesting nanoparticle suitable for use in a nanocomposite consists of an organic chemical/clay intercalate that has been ion-exchanged and reacted and intercalated with one or more quaternary ammonium compounds and an anionic material (such as sodium lauryl sulphate) which is further blended into a polymer resin to make a nanocomposite composition. This material can be blended into a wide variety of polymers. This kind of system disperses well in a number of different types of polymers, and has particular utility in non-polar polymers such as PE and PP.

Another type of intercalate consists of a functional organic monomer having at least one hydroxyl functionality and/or an aromatic ring. The intercalant monomer should preferably include an aromatic ring and/or have a hydroxyl or polyhydroxyl functionality to be sufficiently bound to the clay platelets. Such bonding, via a metal cation of the clay sharing electrons with electronegative atoms of one or two hydroxyl or aromatic ring structures, to an inner surface of the phyllosilicate platelets provides adherence between the intercalant monomer molecules and the platelet inner surfaces of the layered material, and the clay is subsequently exfoliated by processing with a polymer, preferably a polyolefin polymer, and if appropriate, a compatibiliser such as a maleic anhydride-modified polyolefin of the same type as the bulk polymer.

Yet another nanocomposite composition is prepared by co-intercalation of onium ions and an anhydride-curable epoxy resin. The ion-exchange binding between the onium ions and the platelet surface, via ion-exchange with intergallery inorganic cations, eliminates the presence of water molecules associated with the inorganic cations. Therefore, the onium ion-exchange enables the conversion of the hydrophilic interior clay surface to hydrophobic and, therefore, hydrophobic epoxy polymer molecules can then be intercalated into the clay galleries to increase the d-spacing of adjacent layers. The epoxy may, if appropriate, be reacted with a suitable epoxy curing agent added to the bulk polymer, which in turn will assist with the exfoliation when suitably compounded and may further improve the barrier properties of the nanocomposite thus formed as well as improve the adhesion of CVD and traditional varnishes/lacquers to the tube.

Another interesting synergistic intercalant combination consists of a long chain alkyl intercalant and/or an aromatic ring-containing intercalant, both having an electrostatic functionality at a layered material-complexed end of the molecule that is sufficient to provide electrostatic complexing of the intercalant to the interlayer cations on the platelet surface of the layered material, and a matrix polymer-compatible functionality extending from the intercalant molecule or at a free end thereof of the intercalant. Suitable long chain and aromatic ring-containing intercalants include a polar (electrostatic) end having at least one moiety selected from the group consisting of a hydroxyl functionality; a carbonyl functionality; a carboxylic acid or carboxylic acid salt functionality; an amine functionality; an amide functionality; an

ether functionality; an ester functionality; a lactam functionality; a lactone functionality; an anhydride functionality; a nitrile functionality; an n-alkyl halide functionality; a pyridine functionality; a pyrrolidone functionality; a carbon to carbon unsaturated bond (i.e. an alkene or alkyne) and mixtures thereof to sorb or intercalate the intercalant or mixtures of intercalants between adjacent platelets of a layered inorganic material, e.g., a phyllosilicate.

Another interesting synergistic intercalant combination is described in US 6225394, and consists of an alkoxyated onium ion and EVOH. The use of this intercalant combination, and specifically the use of a polymer or other chemical group with good barrier properties that is compatible with the bulk polymer frequently results in significant reductions in OTR of such nanocomposites relative to nanocomposites that don't have such good compatibility with the bulk polymer. Using intercalants that have good barrier properties (eg. EVOH) often results in nanocomposites with improved barrier properties relative to nanocomposites made with intercalants that don't have improved barrier properties. In the case of EVOH, the compatibility of the organo-nanoparticle with, for example, a PE bulk polymer can be improved through the use of EVOH with higher levels of ethylene copolymer; if the level of ethylene copolymer in the EVOH intercalant is high enough, the need for a compatibilising agent to form the nanocomposite may be reduced or even eliminated.

The amount of modified clay material combined with the polymers in a blend should be in an amount that is sufficient to provide the desired ESCR, barrier and/or mechanical properties. The amount of modified clay material in the nanocomposites is generally about 0.1% to about 25% by weight of the composition. A preferred range of modified clay material comprises about 0.5% to about 10% of the composition.

While certain clay minerals have been exemplified above it is understood that any clay mineral (both natural and synthesized) with a large contact area with the polymer to be used in said nanocomposite are useful in tube production. Similarly it is understood that many fine, ultra-fine or nano-sized particle capable of forming a nanocomposite may be useful in the present invention, particularly if it acts as a nucleating agent for one of more of the polymers in the polymer blend.

Polymers suitable for use in the nanocomposites for injection moulded flexible thin walled moulding production are exemplified, but not limited to, polymers such as polyolefins, including plastomers, substantially linear metallocene polyethylene α -olefin copolymers, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), isotactic, syndiotactic and atactic polypropylene (PP) such as polypropylene with varying degrees of isotacticity such as are described in, amongst others, WO 01/27169, WO 99/52955, WO 99/52950 and WO 99/29749, α -olefin copolymers of ethylene, propylene or butene, preferably α -olefin copolymers of ethylene, propylene or butene prepared using metallocene or similar catalysts capable of producing super-random distribution of the α -olefin copolymer within and amongst the molecular chains, polyamides such as poly(m-xylenedipamide) (MXD6), poly(hexamethylenedipamide) and poly(-caprolactam), polyesters such as poly(ethylene terephthalate), and polyacrylonitriles. Other ALOPs and ALOCAs as herein disclosed as well as those discussed in the '255 patent, may be usefully used in the present invention.

Oxygen-scavenging Blends

In yet a further variation of the present invention are blends which incorporate oxygen scavengers or having oxygen scavenging properties. Such blends are useful for the packaging of oxygen-sensitive products. Some of these are described below, but other systems not described may also be suitable.

Note that the present invention is not limited purely to oxygen scavengers. Other types of scavenger, such as aldehyde scavengers, may be used in addition to, or in place of, oxygen scavengers. The precise nature of an alternative scavenger will be dictated by the nature of the component that it is desired to reduce, eliminate or minimise the transmission of through the moulding. An aldehyde scavengers may be useful if, for example, PET or similar is incorporated as a polymer in polymer blends for use in the present invention and causes a problem in terms of increasing the aldehyde content of the material packed into the moulding.

In general, oxygen scavengers consist of oxidisable entities, preferably oxidisable polymers such as polyenes, that are preferably finely dispersed within the bulk polymer. Preferably the oxidisable polymer contains appropriate functionality that makes it compatible or miscible with the bulk polymer. Such functionality may include maleated anhydrides or epoxy functionality. The functionality can be pendant to the backbone or at the chain ends of the polydiene. Preferred functional polydienes include functional polyalkadiene oligomers. Specific non-limiting examples of functional, oxidizable polydienes oxygen scavengers include epoxy functionalized polybutadiene (1,4 and/or 1,2), maleic anhydride grafted or copolymerized polybutadiene (1,4 and/or 1,2), epoxy functionalized polyisoprene, and maleic anhydride grafted or copolymerized polyisoprene.

A milestone in the development of oxygen scavenging polymers was reached by Ching et al., WO 99/48963, which discloses the use of polymers comprising an ethylenic backbone and cycloalkenyl pendant groups, especially polymers comprising cycloalkenyl methyl acrylate or cycloalkenyl methyl methacrylate units, as oxygen scavenging polymers. The cycloalkenyl pendant groups do not generate fragments upon undergoing the scavenging reaction, and thus impart minimal off-taste and malodor to a packaged food or beverage.

The use of pendent cyclic groups containing unsaturation as oxygen scavengers seeks to address the problems associated with scission products of oxygen scavengers by reducing the quantities of scission products. It has been found that when the ethylenic unsaturation is contained within a cyclic group, substantially fewer by-products are produced upon oxidation as compared to analogous non-cyclic materials. Optimally, a packaging material formed from such a composition can retain its physical properties after significant oxygen scavenging. This is particularly beneficial for injection moulded flexible thin walled mouldings because polyolefin compositions have relatively high inherent OTRs and so have the potential to produce a lot of oxidation by-products that may be deleterious to the products packed in containers made therewith.

As an illustration of this development it has been found that materials containing certain cyclohexenyl functionalities are excellent oxygen absorbers when compounded with a transition metal salt and optionally a photoinitiator and that when these materials oxidize they produce very low levels of oxidation by-products. This is in marked contrast to the many non-cyclic-containing oxygen scavengers where excellent oxygen absorbers can be obtained from the use of linear unsaturated compounds compounded with a transition metal salt, and a photoinitiator, but where the levels of oxidation by-products are excessively high. It is thought that this improvement is obtained because mild oxidation of cyclohexene does not break bonds on the ring structure whilst oxidation of a linear unsaturated material under similar conditions produces smaller molecules by chain scission. As a result, they do not require the use of high levels of adjuncts (such as various zeolites) to absorb the undesirable by-products.

A typical oxygen scavenging composition as described above comprises:

- (a) a polymer or lower molecular weight material containing substituted cyclohexene functionality.

(b) a transition metal catalyst such as a salt of a transition metal; and optionally

(c) a photoinitiator. Suitable photoinitiators are well known and some are described in WO 97/07161, WO 97/44364, WO 98/51758, and WO 98/51759.

Another approach is a scavenger composition that includes a transition metal salt and a copolymer (of ethylene and a vinyl monomer) having ether, amino, carboxylic acid, ester, or amide functionalities therefrom. A particularly interesting approach is the use of a variety of ethylenic materials with benzylic or ether containing side chains.

In another variation of the present invention, by selecting appropriate intercalants for the preparation of the organo-clay component of the nanocomposite to be used in the nanocomposite/oxygen scavenger blend it is possible to use as the intercalant a molecule that can also act as an oxygen scavenger. This may be achieved by, for example, selecting as an intercalant an organic molecule that has oxygen scavenging properties or by grafting, polymerising or otherwise incorporating an oxygen scavenging functional group(s) onto a 'standard' (i.e. non-oxygen scavenging) intercalant. For example, polymers grafted or polymerised with polyene oligomers such as butadiene and/or other unsaturated olefins and/or other unsaturated oligomers such as unsaturated cyclic functionalities (eg. cyclohexanyl-containing monomers and oligomers) are frequently capable of reacting with oxygen, said reaction rate frequently being accelerated by the incorporation of suitable catalysts, in particular, transition metals. The optimum level of oxygen scavenging polyene and/or other oxygen scavenging oligomer that is incorporated into a polymer by various means may be determined by experimentation. The optimum level will be influenced by a number of factors, such as the moulding and other physical properties of a polymer or blend at different levels of oligomer incorporation, the degree of oxygen scavenging required by the end use, the activity of the oxygen scavenging component of the blend, the processing conditions required to make the moulded article, etc. Typically, though not necessarily, the oligomer will be present in a 0.1 to 12% range, preferably 2% to 8%.

Polymers grafted or polymerised with polyene oligomers such as butadiene and/or other unsaturated olefins and/or other unsaturated oligomers may also be used as ALOPs, ALOCAs and/or ALOHMFCAs for tube manufacture. Also suitable as polymer components for oxygen scavenging compositions are polymers having an ethylenic or a polyethylenic backbone and moieties which contain a cyclic radical comprising an allylic hydrogen and which are pendant or terminal to the backbone. Preferably the polyolefin is a relatively low molecular weight plastomer, substantially linear polyethylene, metallocene long-chain branched polyethylene or copolymer of the aforementioned ethylene polymers, linear or branched isotactic or syndiotactic polymers, particularly polypropylene and polybutene homopolymers or random copolymers, including linear or branched isotactic or syndiotactic polypropylene homopolymers or random copolymers which have a structure in which their tacticity varies within the range of between 25 and 60% of [mmmm] pentad concentration. Also suitable for use in the present invention are linear or branched isotactic polymers having an arbitrary or rather regular sequence of isotactic and atactic blocks within the polymer molecules.

Another composition of matter having oxygen scavenger capabilities comprises (a) a bulk polymer such as PET, PEN or a polyolefin, (b) a PET, PEN or a polyolefin such as polyethylene or polypropylene containing—usually by grafting—an unsaturated carboxylic anhydride or an unsaturated carboxylic acid, or combinations thereof, or an epoxide; (c) a oxidisable third polymer having OH, SH or NHR₂ groups and (d) a metal salt capable of catalysing the reaction between oxygen and the third polymer. The (grafted) polymer (b) should be present in an amount sufficient so that the blend is non phase-separated. In an example of such a composition the bulk polymer is polyethylene, polyethylene maleic

anhydride is the grafted polymer, the third (oxidisable) polymeric component is MXD6 nylon and the metal is cobalt.

Another type of oxygen scavenger is the use of a (usually aliphatic) polyketone as an oxygen scavenger in a structure for the packaging of oxygen-sensitive products. These utilise the polyketone's high oxygen reactivity to effectively capture any oxygen which may enter the product, thus enhancing the shelf life. The polyketone may be blended or copolymerized with other polymers. For example, a blend comprising 0.1 to 10% by total weight of a polyketone terpolymer scavenger, and the remainder PET, is used to form an injection molded preform and transparent expanded preform beverage bottle.

It is possible to introduce a second olefinic monomer into the polyketone polymerization, such as propylene, which will substitute randomly for ethylene, and in alternation with carbon monoxide, to produce the terpolymer poly(ethylene-alt-carbon monoxide)-stat-(propylene-alt-carbon monoxide) (hereinafter E/P/CO terpolymer. E/P/CO is just one example of a terpolymer, there being many other possible terpolymers with varying properties. Alternatively, it is possible to introduce one or more other olefin monomers that will copolymerize, such as acrylates, methacrylates, alkyl compounds, vinyl acrylate, vinylsilanes, vinyl chloride, etc. Additives such as aldol blocking agents, lubricants, release agents, etc. may be used to enhance processing properties and to reduce the tendency for aldol condensation.

It is known in the art that ascorbate compounds (ascorbic acid, its salts, optical isomers, and derivatives thereof), as well as sulfite salts can be oxidized by molecular oxygen, and can thus serve as components of an oxygen scavenging formulation. The most preferred ascorbate-type oxygen scavenging agents are selected from ascorbate compounds which have limited or no water solubility. The ascorbates and isoascorbates are preferably introduced into the composition as an alkaline earth metal salt or as an ester of a fatty acid or other organic derivative. The oxygen scavenger ascorbate component may be supplemented with other known reducing agents as, for example, a second ascorbate or isoascorbate, tannin, a sulfite salt, and the like. The ascorbate may also be in the form of a C₆-C₂₂ fatty acid ester or diester which may be fully saturated or contain unsaturation in the hydrocarbon chain with a C₁₀-C₂₂ fatty acid ester being preferred. The ascorbate ester may be, for example, ascorbyl laurate, ascorbyl myristate, ascorbyl palmitate, ascorbyl stearate and the like. The saturated acid esters are preferred and most preferred is ascorbyl palmitate.

One or more antioxidants can be incorporated into the scavenging composition of the present invention to retard degradation of the components during compounding and film formation. Although such additives prolong the induction period for oxygen scavenging activity to occur in the absence of irradiation, the article (and any incorporated photoinitiator) can be exposed to radiation at the time oxygen scavenging properties are required.

When an antioxidant is included as part of the composition of the present invention, it preferably is present in an amount which prevents oxidation of the components of the oxygen scavenging composition as well as other materials present in a resultant blend during formation and processing; however, the amount preferably is less than that which interferes with the scavenging activity of the resultant layer, film, or article after initiation has occurred.

Other additives that also can be included in the oxygen scavenging composition of the present invention include, but are not necessarily limited to, fillers, pigments, dyestuffs, processing aids, plasticizers, antifog agents, antiblocking agents, and the like.

Oxygen scavenging components can be used by themselves or as a blend with diluent polymers such as polyolefins and the like and polyesters such as PET, PEN, etc.

Nanocomposite/Oxygen-scavenging Blends

In yet a further development of the present invention it has been found that there is a significant synergistic effect between the nanocomposite and oxygen-scavenging components that result in blends with much better barrier properties than either the equivalent nanocomposite or oxygen scavenging composition on their own.

The incorporation of oxygen scavengers of the present invention into nanocomposites of the present invention significantly enhances the oxygen barrier properties of nanocomposites for a wide variety of applications, including films and other articles made by extrusion or casting, injection stretch, injection blow, thermoforming and other plastic manufacturing processes. The development of nanocomposite/oxygen scavenger blends is particularly, but not exclusively, suited to the injection moulding of injection moulded flexible thin walled mouldings where enhanced oxygen and other barrier properties are required. Virtually all such blends that may be used to form injection moulded flexible thin walled articles, irrespective of polymer type, are suitable for use in nanocomposite/oxygen scavenging blends. For example, polyamides such as the various nylon polymers, polyesters such as PET and PEN, polycarbonates and polyolefins are suited for nanocomposite/oxygen scavenging blends compounds. Polyolefins of various types in particular, by virtue of their relatively low cost and easy processability, are advantageously used for injection moulded flexible thin walled mouldings, and the very good barrier and oxygen scavenging properties of these blends relative to 'standard' polyolefins, polyolefin nanocomposites and polyolefins containing oxygen scavengers when used alone enables the use of polyolefins for applications requiring barrier, particularly to oxygen, for which the aforementioned polyolefins and compositions thereof don't offer sufficiently good barrier properties.

Although the following discussion uses mainly polyolefin nanocomposite/oxygen scavenger compositions as examples, it will be understood that the same principles apply to other polymer types that can be compounded to produce nanocomposite/oxygen scavenger compositions. In the context of nanocomposite/oxygen scavenging discussions, the term 'polyolefin' may therefore be substituted by, for example, polyester (eg. PET, PEN, PBT), polyamide, etc.

There are many oxygen scavenging systems that are suitable for use in blends of the present invention. The suitability of a particular system may be determined by experimentation, as may the optimum type of nanocomposite to be used in conjunction with a particular oxygen scavenger(s) in the invention. Various types of nanocomposites and various methods for their preparation are described in the section on nanocomposite/oxygen scavenging blends compounds, but it will be understood that the types and methods described are non-limiting.

When using nanocomposites for the manufacture of injection moulded flexible thin walled mouldings, either alone or in combination with, for example, oxygen scavengers, the 'Standardised Fill Ratio' for a cavity forming a tube, when expressed in units of mm/sec, is preferably >250, more preferably >300, yet more preferably >400, even more preferably >500, yet even more preferably >700, particularly preferably >800 and most preferably >1000.

Nanocomposite/oxygen scavenging blends are particularly suited to the injection moulding of injection moulded flexible thin walled mouldings, and the nanocomposite/oxygen scavenging compositions display synergistic benefits with regard to barrier properties (measured as OTR) relative to the same essential compositions but in which the nanocomposite and oxygen scavenging components feature as separate components in separate blends. The blends may be prepared by a variety of means, such as by mixing the blend components under high shear mixing conditions or other means capable of producing an intimate mix, such as in a twin-screw extruder. The nanocomposite/oxygen scavenger blend may also be produced by first

preparing a nanocomposite and then as a separate step compounding the oxygen scavenger into the nanocomposite. Alternatively, the polymer/oxygen scavenger blend may be prepared and the organo-clay, or masterbatch thereof, subsequently compounded into the polymer/oxygen scavenger blend. Other means to achieve a well mixed blend will be apparent to those skilled in the art.